Orbital magnetoelectric coupling at finite electric field

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We extend the band theory of linear orbital magnetoelectric coupling to treat crystals under finite electric fields. Previous work established that the orbital magnetoelectric response of a generic insulator at zero field comprises three contributions that were denoted as local circulation, itinerant circulation, and Chern-Simons. We find that the expression for each of them is modified by the presence of a dc electric field. Remarkably, the sum of the three correction terms vanishes, so that the total coupling is still given by the same formula as at zero field. This conclusion is confirmed by numerical tests on a tight-binding model, for which we calculate the field-induced change in the linear magnetoelectric coefficient.

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Magnetoelectrics are magnetic insulators whose dielectric polarization $\mathbf{P}$ changes linearly under a small applied magnetic field $\mathbf{B}$ and, conversely, whose magnetization $\mathbf{M}$ changes linearly with a small applied electric field $\boldsymbol{\mathcal{E}}$.[1,2] This linear magnetoelectric (ME) coupling is described by the response tensor[3]

$$\alpha_{ij} = \frac{\partial M_j}{\partial \mathcal{E}_i} = \frac{\partial P_i}{\partial B_j}, \tag{1}$$

which is odd under both spatial inversion ($\mathcal{P}$) and time-reversal ($\mathcal{T}$) symmetries. Thus ME materials must be acentric and display magnetic order.

In crystals where only one of the two symmetries, $\mathcal{P}$ or $\mathcal{T}$, is present, it may still be possible to induce a linear ME effect by applying an external field which breaks that symmetry. So, for example, a centrosymmetric insulating antiferromagnet placed in a (strong) electric field loses its inversion center. Likewise, a nonmagnetic ferroelectric crystal loses time-reversal symmetry when subject to a magnetic field. In both cases the symmetry is sufficiently lowered that the tensor α becomes nonzero.

It is useful to view these field-induced effects as higher-order ME responses of the unbiased crystal.[4] Two quadratic ME effects can be defined in this way. Going to next order in magnetic field yields the tensor

$$\beta_{ijk} = \frac{\partial \alpha_{ij}}{\partial B_k} = \frac{\partial^2 P_i}{\partial B_j \partial B_k}, \tag{2}$$

which is odd under $\mathcal{P}$ and even under $\mathcal{T}$. Going instead to next order in the electric field gives

$$\gamma_{ijk} = \frac{\partial \alpha_{ji}}{\partial \mathcal{E}_k} = \frac{\partial^2 M_i}{\partial \mathcal{E}_j \partial \mathcal{E}_k}, \tag{3}$$

which is even under $\mathcal{P}$ and odd under $\mathcal{T}$. Reference 4 lists the form of these tensors for all the crystal classes.

While most investigations of ME couplings in solids have focused on the linear response α for a reference state of the crystal at zero electric and magnetic fields, the quadratic responses β and γ have also been measured in materials where α vanishes by symmetry. In particular the electric-field-induced effect, which constitutes the primary focus of this work, was first measured by O'Dell in yttrium iron garnet.[5]

The ME response can be divided into four contributions, depending on whether the response is frozen-ion (purely electronic) or lattice-mediated, and whether it is spin or orbital in character. We will refer to the frozen-ion part of the orbital response as the orbital magneto-electric polarizability (OMP).[6,7] While the OMP is typically a small contribution to the ME response in conventional magnetoelectrics, it was recently realized that, under certain conditions of surface preparation, $\mathbb{Z}_2$-odd topological insulators[8] should display a large, quantized OMP response.[6,9] This is a remarkable prediction, especially considering that in this class of materials $\mathcal{T}$ symmetry is preserved in the bulk (it must, however, be broken on the surface). This topological magnetoelectric effect has triggered a great deal of interest in orbital magneto-electric couplings in solids.

The microscopic theory needed to calculate the OMP at zero electric and magnetic fields from first principles was worked out in Refs. 7 and 10. In addition to the so-called Chern-Simons term responsible for the topological ME effect,[6,9,11] it was found that two more (Kubo) terms contribute to the OMP in conventional magnetoelectrics in which $\mathcal{T}$ and $\mathcal{P}$ symmetries are broken spontaneously in the bulk.

In this work we generalize the band theory of OMP of periodic insulators[7,10] to finite electric fields. That is, we

evaluate the coefficient α at nonzero $\boldsymbol{\mathcal{E}}$,

$$\alpha_{ij}(\boldsymbol{\mathcal{E}}) = \frac{\partial M_j}{\partial \mathcal{E}_i}\bigg|_{\mathbf{B}=0}. \tag{4}$$

(Henceforth, the condition $\mathbf{B} = 0$ will be implied throughout. It is also understood that from now on α denotes the OMP part of the entire ME response.) A principal result of our work is the conclusion that the zero-field expression for the *total* OMP remains valid at finite electric field, while the above-mentioned Chern-Simons and Kubo terms separately acquire field-induced contributions. We confirm our formal results by numerical tests on a tight-binding model.

Our derivation of a formula for $\alpha(\boldsymbol{\mathcal{E}})$ proceeds along the lines of Ref. 7. We start from the expression given therein for the orbital magnetization of a generic band insulator under a finite electrical bias. It comprises three terms,

$$M_j(\boldsymbol{\mathcal{E}}) = M_j^{\mathrm{LC}}(\boldsymbol{\mathcal{E}}) + M_j^{\mathrm{IC}}(\boldsymbol{\mathcal{E}}) + M_j^{\mathrm{CS}}(\boldsymbol{\mathcal{E}}), \tag{5}$$

where

$$M_j^{\mathrm{LC}} = -\frac{\eta}{2}\epsilon_{jpq}\int d^3k\,\mathrm{Im}\,\langle\widetilde{\partial}_p u_{n\mathbf{k}}|H_{\mathbf{k}}^0|\widetilde{\partial}_q u_{n\mathbf{k}}\rangle, \tag{6}$$

$$M_j^{\mathrm{IC}} = -\frac{\eta}{2}\epsilon_{jpq}\int d^3k\,\mathrm{Im}\,\left\{\langle u_{n\mathbf{k}}|H_{\mathbf{k}}^0|u_{m\mathbf{k}}\rangle\langle\widetilde{\partial}_p u_{m\mathbf{k}}|\widetilde{\partial}_q u_{n\mathbf{k}}\rangle\right\}, \tag{7}$$

and

$$M_j^{\mathrm{CS}} = \frac{e\eta}{2}\mathcal{E}_j\int d^3k\,\epsilon_{pqr}\mathrm{tr}\left[A_p\partial_q A_r - \frac{2i}{3}A_p A_q A_r\right]. \tag{8}$$

The common prefactor in these formulas is $\eta = -e/\hbar(2\pi)^3$ ($e > 0$ is the magnitude of the electron charge), and a sum is implied over repeated Cartesian (pqr) and valence-band (mn) indices. The cell-periodic part of the field-polarized Bloch state[12] is denoted by $|u_{n\mathbf{k}}\rangle$, ∂_j is the partial derivative with respect to the jth component of the wavevector $\mathbf{k}$, and the tilde indicates a covariant derivative $\widetilde{\partial}_j = Q_{\mathbf{k}}\partial_j$, where $Q_{\mathbf{k}} = 1 - |u_{n\mathbf{k}}\rangle\langle u_{n\mathbf{k}}|$ (sum implied over n). The Hamiltonian $H_{\mathbf{k}}^0$ is defined as

$$H_{\mathbf{k}}^0 = e^{-i\mathbf{k}\cdot\mathbf{r}}\mathcal{H}^0 e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{9}$$

where $\mathcal{H}^0$ is the zero-field part of the crystal Hamiltonian. In Eq. (8) the symbol A_p denotes the Berry connection matrix

$$A_{mn\mathbf{k}p} = i\langle u_{m\mathbf{k}}|\partial_p u_{n\mathbf{k}}\rangle, \tag{10}$$

and the trace is over the valence bands.

Equations (6) and (7) describe respectively the *local* and *itinerant* circulation contributions to the magnetiztion,[7] while Eq. (8) is the Chern-Simons term. At variance with the other two terms, whose dependence on the electric field is only implicit, $\mathbf{M}^{\mathrm{CS}}$ displays an explicit linear dependence on $\boldsymbol{\mathcal{E}}$. It is therefore expedient to introduce a new quantity M_1^{CS} via the relation

$$M_j^{\mathrm{CS}}(\boldsymbol{\mathcal{E}}) \equiv \mathcal{E}_j M_1^{\mathrm{CS}}(\boldsymbol{\mathcal{E}}), \tag{11}$$

where the subscript '1' serves as a reminder that M_1^{CS} enters the expression for $\mathbf{M}$ multiplied by $\boldsymbol{\mathcal{E}}$ to the first power.

All three magnetization terms, $\mathbf{M}^{\mathrm{LC}}$, $\mathbf{M}^{\mathrm{IC}}$, and $\mathbf{M}^{\mathrm{CS}}$, are invariant under gauge transformations within the valence-band manifold, although in the case of $\mathbf{M}^{\mathrm{CS}}$ this invariance is only modulo a quantum of indeterminacy.[9] In the limit that $\boldsymbol{\mathcal{E}}$ goes to zero, $\mathbf{M}^{\mathrm{CS}}$ vanishes and Eq. (5) reduces to the expression for the spontaneous orbital magnetization.[13]

As already mentioned, all terms in Eq. (5) can contribute to the linear ME coupling, Eq. (4), so that

$$\alpha_{ij}(\boldsymbol{\mathcal{E}}) = \alpha_{ij}^{\mathrm{LC}}(\boldsymbol{\mathcal{E}}) + \alpha_{ij}^{\mathrm{IC}}(\boldsymbol{\mathcal{E}}) + \alpha_{ij}^{\mathrm{CS}}(\boldsymbol{\mathcal{E}}). \tag{12}$$

The derivation of the expressions for these objects is straightforward though somewhat lengthy. It essentially repeats the steps in Appendix B of Ref. 7, where the derivation was carried out for the LC and IC ("Kubo") terms under the assumption that $\boldsymbol{\mathcal{E}} = 0$ (the CS term is trivial at $\boldsymbol{\mathcal{E}} = 0$). At $\boldsymbol{\mathcal{E}} \neq 0$ one may show that each of the terms in Eq. (12) consists of a "zero-field" part plus a "field-correction" part having an explicit linear dependence on $\boldsymbol{\mathcal{E}}$,

$$\alpha_{ij}(\boldsymbol{\mathcal{E}}) = \alpha_{0,ij}(\boldsymbol{\mathcal{E}}) + \mathcal{E}_j\alpha_{1,i}(\boldsymbol{\mathcal{E}}). \tag{13}$$

The field-correction terms for the LC and IC contributions can be traced back to Eqs. (B.7) and (B.8) in Ref. 7, which at $\boldsymbol{\mathcal{E}} \neq 0$ acquire extra terms. As for the Chern-Simons contribution, differentiating Eq. (11) with respect to $\mathcal{E}_j$ yields $\alpha_{0,ij}^{\mathrm{CS}} = \delta_{ij}M_1^{\mathrm{CS}}$ and $\alpha_{1,i}^{\mathrm{CS}} = \partial M_1^{\mathrm{CS}}/\partial\mathcal{E}_i$.

Thus, we arrive at the results

$$\alpha_{0,ij}^{\mathrm{LC}}(\boldsymbol{\mathcal{E}}) = \eta\epsilon_{jpq}\mathrm{Im}\int d^3k\left(\langle\widetilde{\partial}_p u_{n\mathbf{k}}|(\partial_q H_{\mathbf{k}}^0)|\widetilde{D}_i u_{n\mathbf{k}}\rangle\right.$$
$$\left.-\frac{1}{2}\langle\widetilde{\partial}_p u_{n\mathbf{k}}|(D_i H_{\mathbf{k}}^0)|\widetilde{\partial}_q u_{n\mathbf{k}}\rangle\right), \tag{14}$$

$$\alpha_{0,ij}^{\mathrm{IC}}(\boldsymbol{\mathcal{E}}) = \eta\epsilon_{jpq}\mathrm{Im}\int d^3k\left(\langle\widetilde{\partial}_p u_{n\mathbf{k}}|\widetilde{D}_i u_{m\mathbf{k}}\rangle\langle u_{m\mathbf{k}}|(\partial_q H_{\mathbf{k}}^0)|u_{n\mathbf{k}}\rangle\right.$$
$$\left.-\frac{1}{2}\langle\widetilde{\partial}_p u_{n\mathbf{k}}|\widetilde{\partial}_q u_{m\mathbf{k}}\rangle\langle u_{m\mathbf{k}}|(D_i H_{\mathbf{k}}^0)|u_{n\mathbf{k}}\rangle\right), \tag{15}$$

$$\alpha_{0,ij}^{\mathrm{CS}}(\boldsymbol{\mathcal{E}}) = \delta_{ij}\eta\frac{e}{2}\int d^3k\,\epsilon_{pqr}\mathrm{tr}\left[A_p\partial_q A_r - \frac{2i}{3}A_p A_q A_r\right], \tag{16}$$

$$\alpha_{1,i}^{\mathrm{LC}}(\boldsymbol{\mathcal{E}}) = \eta e\int d^3k\,\epsilon_{pqr}\mathrm{Re}\left[\langle\widetilde{D}_i u_{n\mathbf{k}}|\widetilde{\partial}_p u_{m\mathbf{k}}\rangle\langle\widetilde{\partial}_q u_{m\mathbf{k}}|\widetilde{\partial}_r u_{n\mathbf{k}}\rangle\right], \tag{17}$$

and

$$\alpha_{1,i}^{\mathrm{LC}}(\boldsymbol{\mathcal{E}}) = \alpha_{1,i}^{\mathrm{IC}}(\boldsymbol{\mathcal{E}}) = -\frac{1}{2}\alpha_{1,i}^{\mathrm{CS}}. \qquad (18)$$

In the above expressions, D_i is the partial derivative with respect to the ith component of the electric field. The terms containing $D_i H_{\mathbf{k}}^0$ in Eqs. (14) and (15) are screening corrections which are present in self-consistent calculations.

Equations (14)–(16) for the zero-field terms are essentially rewritten from Ref. 7. It should be emphasized, however, that in the present context these expressions depend on the electric field implicitly via the wave functions. The explicit field dependence is given by the field-correction terms, Eqs. (17) and (18). Remarkably, these terms are not independent and add up to zero when inserted into Eq. (12). We conclude, therefore, that the expression for the *total* OMP derived in Refs. 7 and 10 assuming $\boldsymbol{\mathcal{E}} = 0$ remains valid for $\boldsymbol{\mathcal{E}} \neq 0$. This constitutes one of our principal results. The explicit expression given in Eq. (17) for the field-correction terms is the other main result of this work. It is useful if one is interested in the field dependence of the separate gauge-invariant contributions to the OMP. Because it contains three k derivatives and one field derivative, this quantity is even under $\mathcal{P}$ and odd under $\mathcal{T}$, just like the coefficient γ defined by Eq. (3). This is reasonable since, as one can see from Eq. (13), $\alpha_1^{\mathrm{LC/IC/CS}}$ gives a contribution to $\gamma^{\mathrm{LC/IC/CS}}$ and should therefore have the same symmetry properties.

As a check of our analytic derivation, we have implemented the formula for $\alpha(\boldsymbol{\mathcal{E}})$ in a tight-binding model, and used it to calculate the nonlinear ME coefficient γ_{zzz} at $\boldsymbol{\mathcal{E}} = 0$. Since the tensor γ vanishes in $\mathcal{T}$-invariant systems, we need a model where $\mathcal{T}$ is spontaneously broken, and we chose that of Ref. 7. This is a spinless model with eight sites per primitive cell arranged on a $2 \times 2 \times 2$ cube, where $\mathcal{T}$ symmetry is broken by complex nearest-neighbor hoppings, and we have used the same on-site energies and nearest-neighbor hoppings tabulated in that work. (This choice of parameters also breaks $\mathcal{P}$, so that the linear ME tensor α is nonzero already at $\boldsymbol{\mathcal{E}} = 0$, but this is not essential for our present purposes.) As in Ref. 7 the two lowest bands were treated as occupied, and the phase φ of one of the complex hoppings was chosen as a control parameter for plotting purposes.

The technical details of the tight-binding implementation of Eqs. (6)–(8) and (14)–(17) can be found in Ref. 7. The only significant difference with respect to that work is that the field derivative $|\widetilde{D}_i u_{n\mathbf{k}}\rangle$ of the cell-periodic Bloch states must be evaluated at *finite* $\boldsymbol{\mathcal{E}}$. Under these circumstances the usual "sum-over-states" formula[13] cannot be employed, and one must instead minimize a suitably defined functional.[14]

We shall calculate the zzz component of γ from the first equality in Eq. (3). Combining with Eq. (12) we find

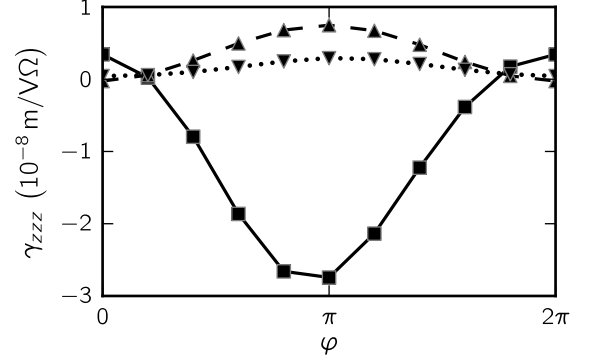$$\gamma = \gamma^{\mathrm{LC}} + \gamma^{\mathrm{IC}} + \gamma^{\mathrm{CS}}. \qquad (19)$$

FIG. 1. Decomposition of γ_{zzz} of Eq. (19) into γ^{LC} (solid lines), γ^{IC} (dashed lines), and γ^{CS} (dotted lines) calculated using Eqs. (20) and (21). Symbols denote the same contributions evaluated using Eq. (22).

The CS term is the simplest to evaluate, as the derivative of Eq. (13) with respect to $\mathcal{E}_z$ can be taken analytically. The zero-field and field-correction terms therein both contribute an amount $\alpha_{1,z}^{\mathrm{CS}}(0)$ to $\gamma_{zzz}^{\mathrm{CS}}(0)$. Thus,

$$\gamma_{zzz}^{\mathrm{CS}}(0) = 2\alpha_{1,z}^{\mathrm{CS}}(0) = -4\alpha_{1,z}^{\mathrm{LC}}(0), \qquad (20)$$

where the second equality follows from Eq. (18). The quantity on the right-hand side can be evaluated directly from Eq. (17). For the LC and IC terms we calculate the derivative of the zero-field terms in Eq. (13) using finite differences and obtain

$$\gamma_{zzz}^{\mathrm{LC/IC}}(0) \simeq \frac{\alpha_{0,zz}^{\mathrm{LC/IC}}(\mathcal{E}_z) - \alpha_{0,zz}^{\mathrm{LC/IC}}(-\mathcal{E}_z)}{2\mathcal{E}_z} + \alpha_{1,z}^{\mathrm{LC}}(0). \quad (21)$$

In practice we evaluate the first term from Eqs. (14) and (15), using small positive and negative fields along z of magnitude $\mathcal{E}_z = 1.0 \times 10^{-5}\,\mathrm{V/m}$.

The results of the above calculations were compared with a finite-difference determination of the second field derivative of $\mathbf{M}$,

$$\gamma_{zzz}(0) = \left.\frac{\partial^2 M_z}{\partial \mathcal{E}_z^2}\right|_{\boldsymbol{\mathcal{E}}=0} \simeq \frac{M_z(\mathcal{E}_z) - 2M_z(0) + M_z(-\mathcal{E}_z)}{\mathcal{E}_z^2}, \qquad (22)$$

using the k-space expressions from Ref. 7 for the LC, IC and CS terms in Eq. (5). The results obtained in this manner can be taken as a reference, since the k-space expression for $\mathbf{M}(\boldsymbol{\mathcal{E}})$ has been carefully tested by comparing with real-space calculations on bounded samples cut from the bulk crystal.[7]

The agreement between the two sets of calculations can be seen in Fig. 1, where the LC, IC, and CS contributions to γ_{zzz} are plotted separately as functions of φ. In this calculation $\gamma_{zzz}^{\mathrm{CS}}$ is about an order of magnitude smaller than $\gamma_{zzz}^{\mathrm{LC}}$. From Eqs. (20) and (21) it then follows that the field-correction terms contribute little, especially in the case of $\gamma_{zzz}^{\mathrm{LC}}$. Further numerical tests focusing on those small terms are therefore desirable.
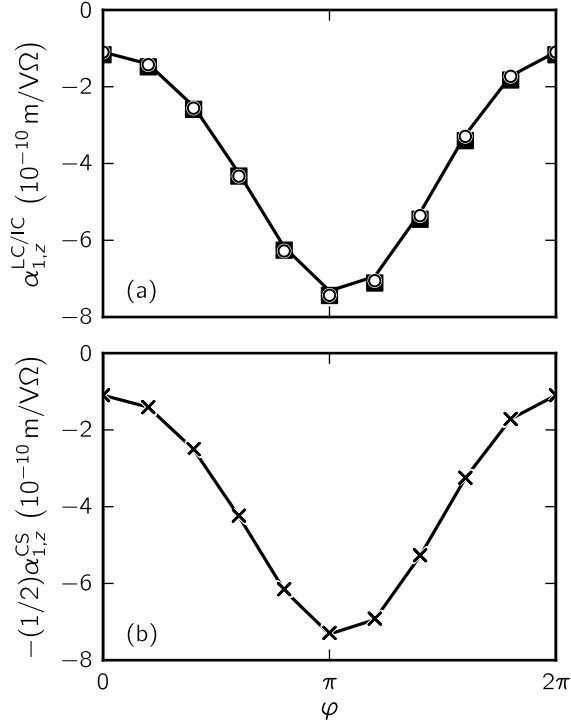
FIG. 2. (a) Right-hand side (solid line) and left-hand side (symbols) of Eq. (23). Squares and circles denote the LC and IC contributions, respectively. (b) Equation (20) (solid line) and Eq. (22) for the CS contribution (crosses), both multiplied by a factor of $-1/4$ for visual check of Eq. (18) by comparison to (a).

In order to isolate the field-correction terms in $\gamma_{zzz}^{\mathrm{LC}}$ and $\gamma_{zzz}^{\mathrm{IC}}$, we subtract the zero-field terms from the total:

$$\left[\frac{\partial^2 M_z^{\mathrm{LC/IC}}}{\partial \mathcal{E}_z^2} - \frac{\partial \alpha_{0,zz}^{\mathrm{LC/IC}}}{\partial \mathcal{E}_z}\right]_{\boldsymbol{\mathcal{E}}=0} = \alpha_{1,z}^{\mathrm{LC/IC}}(0). \qquad (23)$$

In Fig. 2 (a) we plot, as a function of φ, the two sides of this equation. The field derivatives on the left-hand side are evaluated by finite differences, while the right-hand side is calculated from Eq. (17). It is clear that the field-correction terms in Eq. (13) are nonzero, and the good agreement between the three curves demonstrates that for both LC and IC they are given by Eq. (17).

The CS contribution does not need additional tests since, as noted above, the contributions to $\gamma_{zzz}^{\mathrm{CS}}$ from the zero-field and field-correction terms are identical. However, we reproduce in Fig. 2 (b) the CS curve from Fig. 1 multiplied by a factor $-1/4$, so that the correctness of Eq. (18) can be verified by direct visual inspection. This completes the numerical checks of the k-space formula for $\alpha(\boldsymbol{\mathcal{E}})$.

To summarize, we have extended the recently developed band theory of orbital magnetoelectric response to treat crystals under a finite electrical bias. The theory presented in this work may be especially useful in calculations of the second-order magnetoelectric effect defined by Eq. (3). While it is possible in principle to calculate the second derivative of $\mathbf{M}$ by finite differences, the numerical stability is likely to be improved by taking one of the field derivatives analytically, leaving only one derivative to be performed numerically. We have demonstrated that in order to calculate the *total* OMP at finite electric field, one may use the same equations (14)–(16) that were previously derived for zero field. This is true even though the individual local-circulation, itinerant-circulation, and Chern-Simons contributions do separately acquire field-correction terms. At present, we are not aware of any simple argument that could have anticipated the exact cancellation of these terms in the expression for the total OMP.

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